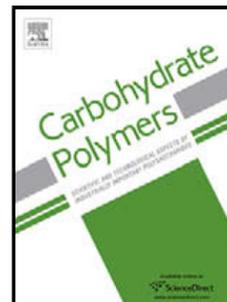


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1 **Characteristics of starch-based films with different amylose contents**  
2 **plasticised by 1-ethyl-3-methylimidazolium acetate**

3

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17 **ABSTRACT**

18 Starch-based films plasticised by an ionic liquid, 1-ethyl-3-methylimidazolium  
19 acetate ([Emim][OAc]), were prepared by a simple compression moulding process,  
20 facilitated by the strong plasticisation effect of [Emim][OAc]. The effects of amylose  
21 content of starch (regular vs. high-amylose maize) and relative humidity (RH) during  
22 ageing of the samples on a range of structural and material characteristics were  
23 investigated. Surprisingly, plasticisation by [Emim][OAc] made the effect of amylose  
24 content insignificant, contrary to most previous studies when other plasticisers were used.  
25 In other words, [Emim][OAc] changed the underlying mechanism responsible for  
26 mechanical properties from the entanglement of starch macromolecules (mainly  
27 amylose), which has been reported as a main responsible factor previously. The  
28 crystallinity of the plasticised starch samples was low and thus was unlikely to have a  
29 major contribution to the material characteristics, although the amylose content impacted  
30 on the crystalline structure and the mobility of amorphous parts in the samples to some  
31 extent. Therefore, RH conditioning and thus the sample water content was the major  
32 factor influencing the mechanical properties, glass transition temperature, and electrical  
33 conductivity of the starch films. This suggests the potential application of ionic liquid-  
34 plasticised starch materials in areas where the control of properties by environmental RH  
35 is desired.

36

37 *Keywords:*

38 Starch; Ionic liquid; 1-Ethyl-3-methylimidazolium acetate; Plasticization;

39 Amylose/amylopectin ratio; Relative Humidity; Electrical Conductivity

40

41 Chemical compounds studied in this article

42 Starch (PubChem CID: 24836924); Water (PubChem CID: 962); Glycerol (PubChem

43 CID: 753); 1-Ethyl-3-methylimidazolium acetate (PubChem CID: 11658353)

44

45 **1. Introduction**

46 In recent years, great attention has been focused on polymers from renewable  
47 resources (biopolymers: cellulose, starch, chitosan, chitin, etc.; bio-based polymers:  
48 poly(lactic acid) (PLA), polyhydroxyalkanoates (PHA), etc.) due to their availability,  
49 renewability, biocompatibility, and biodegradability (Yu, Dean, & Li, 2006). Among  
50 these groups of polymers, starch grows in plants and is naturally structured in a  
51 hierarchical multi-level complex form: from macro-observation, starch is in the form of  
52 granules ( $<1\ \mu\text{m}\sim 100\ \mu\text{m}$ ); many granules are broadly composed of alternating  
53 amorphous and semicrystalline shells (growth rings) ( $100\sim 400\ \text{nm}$ ); the semicrystalline  
54 shell is stacked crystalline and amorphous lamellae (periodicity) ( $9\sim 10\ \text{nm}$ ); with all  
55 structures based on two major biomacromolecules called amylose (mainly linear) and  
56 amylopectin (hyper-branched) ( $\sim\text{nm}$ ) (Fu, Wang, Li, Wei, & Adhikari, 2011; Jane, 2009;  
57 Pérez, Baldwin, & Gallant, 2009; Pérez & Bertoft, 2010). For the utilisation of starch, it  
58 is important to understand this complex structure and how it can be altered to achieve  
59 desired forms (e.g. a plasticised form).

60 With a plasticiser and elevated temperature, a process known as “gelatinisation” (with  
61 abundant plasticiser content) or “melting” (with limited plasticiser content) occurs,  
62 resulting in disruption of the 3D structure of native starch; and, if preferential conditions

63 are reached, this can result in a homogeneous amorphous material known as  
64 “thermoplastic starch” or “plasticised starch”, which is essential in the production of  
65 some starch-based materials (Avérous, 2004; Liu, Xie, Yu, Chen, & Li, 2009a; Xie,  
66 Halley, & Avérous, 2012; Xie, Pollet, Halley, & Avérous, 2013). While water is the  
67 most commonly used plasticiser for starch, substances such as polyols (glycerol, glycol,  
68 sorbitol, etc.), compounds containing nitrogen (urea, ammonium derived, amines), and  
69 citric acid have also been reported to be effective in the plasticisation of starch (Liu et al.,  
70 2009a; Xie et al., 2012). A plasticiser for starch should preferably be stable (non-volatile)  
71 both during thermal processing and in post-processing stages, be ineffective in starch  
72 macromolecular degradation, be safe to humans and the environment, and be able to  
73 provide starch-based materials with enhanced performance and new capabilities.  
74 Unfortunately, the currently-used plasticisers do not yet have all the desired attributes and  
75 thus finding alternative and better plasticisers for starch is of interest.

76 Ionic liquids, often referred to as “green solvents”, have the capability of dissolving  
77 many substances, including many organic polymers, and have good properties such as  
78 chemical and thermal stability, low vapour pressure, and high ionic activity (Lu, Yan, &  
79 Texter, 2009). Many ILs, especially ones based on the imidazolium cation, have been  
80 shown to be capable of dissolving polysaccharides such as starch (Biswas, Shogren,  
81 Stevenson, Willett, & Bhowmik, 2006; El Seoud, Koschella, Fidale, Dorn, & Heinze,  
82 2007; Wilpiszewska & Szychaj, 2011; Zakrzewska, Bogel-Lukasik, & Bogel-Lukasik,  
83 2010; Zhu et al., 2006), cellulose (Heinze, Schwikal, & Barthel, 2005; Zhang, Wu, Zhang,  
84 & He, 2005), chitin/chitosan (Wu, Sasaki, Irie, & Sakurai, 2008; Xie, Zhang, & Li, 2006),  
85 silk fibroin (Phillips et al., 2004; Wang, Chen, Yang, & Shao, 2012; Wang, Yang, Chen,

86 & Shao, 2012), lignin (Pu, Jiang, & Ragauskas, 2007), zein protein (Biswas et al., 2006),  
87 wool keratin (Xie, Li, & Zhang, 2005); and thus can be used as excellent media for  
88 polysaccharide plasticisation and modification. Moreover, the use of ILs may also allow  
89 for the development of starch-based ionically conducting polymers or solid polymer  
90 electrolytes (Liew, Ramesh, Ramesh, & Arof, 2012; Ramesh, Liew, & Arof, 2011;  
91 Ramesh, Shanti, Morris, & Durairaj, 2011; Ramesh, Shanti, & Morris, 2012; Wang,  
92 Zhang, Liu, & He, 2009a; Wang, Zhang, Wang, & Liu, 2009b; Wang, Zhang, Liu, &  
93 Han, 2010b). Nevertheless, work reported to date mostly involved processing in solution,  
94 whereas melt processing should be more relevant to industry application as much less  
95 solvent is required and higher efficiency is expected. Sankri et al. (2010) and Leroy,  
96 Jacquet, Coativy, Reguerre, and Lourdin (2012) have done pioneering work using an IL  
97 (1-butyl-3-methylimidazolium chloride, or [Bmim][Cl]) as a new plasticiser for melt  
98 processing of starch-based materials, which demonstrated improved plasticisation,  
99 electrical conductivity, and hydrophobicity. Our previous work (Xie et al., 2014) has  
100 shown that an IL, 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]), has a significant  
101 plasticisation effect including for a high-amylose starch, prepared via a simple  
102 compression moulding process; and can reduce the crystallinity and make the amorphous  
103 phase more mobile, advantageous for some specific applications (e.g. electrically  
104 conductive materials).

105 This paper reports studies aimed at understanding the plasticisation effect of starch by  
106 ILs. Based on the established protocol (Xie et al., 2014), we investigate how the amylose  
107 content of starch can influence the characteristics of starch-based materials plasticised by  
108 the IL, [Emim][OAc]. It is well established that the amylose content can greatly

109 influence starch granule architecture and molecular structure (Blazek et al., 2009;  
110 Cheetham & Tao, 1997; Jenkins & Donald, 1995; Shi, Capitani, Trzasko, & Jeffcoat,  
111 1998), thermal behaviour (Liu, Yu, Xie, & Chen, 2006; Liu et al., 2011), processing and  
112 rheological behaviour (Chaudhary, Miler, Torley, Sopade, & Halley, 2008; Chinnaswamy  
113 & Hanna, 1988; Della Valle, Colonna, Patria, & Vergnes, 1996; Li et al., 2011; Wang et  
114 al., 2010a; Xie et al., 2009), and the structure and properties of resulting starch-based  
115 materials (Chaudhary, Torley, Halley, McCaffery, & Chaudhary, 2009; Cheetham & Tao,  
116 1998; Forssell, Lahtinen, Lahelin, & Myllärinen, 2002; Li et al., 2011; Lourdin, Della  
117 Valle, & Colonna, 1995; Mondragón, Mancilla, & Rodríguez-González, 2008; Rindlav-  
118 Westling, Stading, & Gatenholm, 2001; Rindlav-Westling, Stading, Hermansson, &  
119 Gatenholm, 1998; van Soest & Borger, 1997). In order to reveal the effect of amylose  
120 content in the current study, a simple one-step compression moulding process was  
121 employed to minimise the effect of shear-induced macromolecular degradation during  
122 processing. Moreover, considering that starch is a hydrophilic biopolymer sensitive to  
123 environmental moisture and that [Emim][OAc], an hydrophilic IL, may have some  
124 impact on the hydrophilicity of starch-based materials, the effect of relative humidity  
125 (RH) during ageing of the materials on the material characteristics was also investigated.  
126 Thus, the plasticisation effects of [Emim][OAc] on the crystalline structure, mechanical  
127 properties, glass transition temperature, thermal stability, and electrical conductivity of  
128 the starch-based films are reported here, with the aim of providing information for  
129 designing starch plasticisation processes and starch-based materials with tailored  
130 properties.  
131

## 132 2. Materials and Methods

### 133 2.1. Materials

134 Two commercially available maize starches, Gelose 80 (G80) and regular maize  
135 starch (RMS) were used in this work. RMS was supplied by New Zealand Starch Ltd.  
136 (Onehunga, Auckland, New Zealand) with the product name Avon Maize Starch; and  
137 G80 was supplied by Ingredion ANZ Pty Ltd (Lane Cove, NSW, Australia). Both  
138 starches were chemically unmodified and their amylose contents were 24.4% and 82.9%,  
139 respectively, as measured previously (Tan, Flanagan, Halley, Whittaker, & Gidley, 2007).  
140 The original moisture content of the two starches were 14.1 wt.% and 14.4 wt.%  
141 respectively, as measured by a Satorius Moisture Analyser (Model MA30, Sartorius  
142 Weighing Technology GmbH, Weender Landstraße 94–108, 37075, Goettingen,  
143 Germany). Deionised water was used in all instances. Glycerol (AR) was supplied by  
144 Chem-Supply Pty Ltd (Gillman, SA, Australia) and used as received. [Emim][OAc] of  
145 purity  $\geq 95\%$ , produced by IoLiTec Ionic Liquids Technologies GmbH (Salzstraße 184,  
146 D-74076 Heilbronn, Germany), was also supplied by Chem-Supply Pty Ltd.  
147 [Emim][OAc] was used as received without further purification. As [Emim][OAc] was  
148 liquid at room temperature miscible with water (Mateyawa et al., 2013), different ratios  
149 of water–[Emim][OAc] mixture could be easily prepared in vials for subsequent use.

150

### 151 2.2. Sample preparation

152 Formulations for sample preparation are shown in Table 1. In Table 1 and the  
153 following text, the plasticised starch samples are coded in the format of “G80-18-L”,  
154 where “G80” denotes the type of starch, “18” indicates the weight content of the ionic

155 liquid, and “L” means the RH during conditioning (either L, low, 33%; M, medium, 52%;  
156 or H, high, 75%). Based on our preliminary work (Xie et al., 2014), the added water–  
157 [Emim][OAc] mixture content was fixed at 30% by weight on the basis of the starch wet  
158 weight. The liquid mixture was added drop-wise to the starch, accompanied by careful  
159 blending using a mortar and pestle to ensure an even distribution of the liquid mixture in  
160 the starch. Then, the blended samples were hermetically stored in ziplock bags at 4 °C  
161 for at least overnight, before thermal compression moulding. This allowed time for  
162 further equilibration of the samples. The powder was carefully and equally spread over  
163 the moulding area with poly(tetrafluoroethylene) glass fabrics (Dotmar EPP Pty Ltd,  
164 Acacia Ridge, Qld, Australia) located between the starch and the mould, then  
165 compression moulded at 160 °C and 6 MPa for 10 min, followed by rapidly cooling to  
166 room temperature (RT) before opening the mould and retrieving the sample (thickness  
167 approx. 1.2 mm). The films were conditioned at different RHs, 33% (over saturated  
168 magnesium chloride solution), 52% (over saturated magnesium nitrate solution), and 75%  
169 (over saturated sodium chloride solution), at RT in desiccators for one month before any  
170 characterisation of the materials. After the conditioning, the thickness of the films was  
171 about 1 mm. The final water contents in the conditioned samples were calculated based  
172 on the weight data before and after vacuum-oven drying at 100 °C for two days.

173

174

175 [Insert Table 1 here]

176

177

178 According to our preliminary work (Xie et al., 2014), the use of compression  
179 moulding under the described conditions should mostly destroy the starch granules so  
180 that plasticised starch could be formed.

181

## 182 2.3. Characterisation

### 183 2.3.1. X-ray diffraction (XRD)

184 The starch samples were placed in the sample holder of a powder X-ray  
185 diffractometer (D8 Advance, Bruker AXS Inc., Madison, WI, USA) equipped with a  
186 graphite monochromator, a copper target, and a scintillation counter detector. XRD  
187 patterns were recorded for an angular range ( $2\theta$ ) of 4–40°, with a step size of 0.02° and a  
188 step rate of 0.5 s per step, and thus the scan time lasted for approximately 15 min. The  
189 radiation parameters were set as 40 kV and 30 mA, with a slit of 2 mm. Traces were  
190 processed using the Diffracplus Evaluation Package (Version 11.0, Bruker AXS Inc.,  
191 Madison, WI, USA) to determine the X-ray diffractograms of the samples. The degree of  
192 crystallinity was calculated using the method of Lopez-Rubio, Flanagan, Gilbert, and  
193 Gidley (2008) with the PeakFit software (Version 4.12, Systat Software, Inc., San Jose,  
194 CA, USA), Eq. (1):

195

$$196 \quad X_c = \frac{\sum_{i=1}^n A_{ci}}{A_t} \quad (1)$$

197

198 where  $A_{ci}$  is the area under each crystalline peak with index  $i$ , and  $A_t$  is the total area (both  
199 amorphous background and crystalline peaks) under the diffractogram.

200 The V-type crystallinity (single-helical amylose structure) was calculated based on  
201 the total crystalline peak areas at 7.5, 13, 20, and 23° (van Soest, Hulleman, de Wit, &  
202 Vliegthart, 1996).

203

### 204 2.3.2. NMR

205 The rigid components (short-range orders and rigid amorphous starch) of the starch-  
206 based films were examined by solid-state  $^{13}\text{C}$  cross-polarization magic angle spinning  
207 nuclear magnetic resonance ( $^{13}\text{C}$  CP/MAS NMR) experiments at a  $^{13}\text{C}$  frequency of  
208 75.46 MHz on a Bruker MSL-300 spectrometer. Using scissors, the sheets were cut into  
209 small evenly sized pieces and were packed in a 4-mm diameter, cylindrical, PSZ  
210 (partially-stabilized zirconium oxide) rotor with a Kelf end cap. The rotor was spun at  
211 5 kHz at the magic angle (54.7°). The 90° pulse width was 5  $\mu\text{s}$  and a contact time of  
212 1 ms was used for all samples with a recycle delay of 3 s. The spectral width was 38 kHz,  
213 acquisition time 50 ms, time domain points 2 k, transform size 4 k, and line broadening  
214 50 Hz. At least 2400 scans were accumulated for each spectrum. Spectra were  
215 referenced to external adamantane and analysed by resolving the spectra into ordered and  
216 amorphous sub-spectra and calculating the relative areas as described previously (Tan et  
217 al., 2007).

218 The amounts of “mobile amorphous starch” and “rigid amorphous starch” were  
219 calculated according to our method reported previously (Xie et al., 2014). Briefly, it was  
220 assumed that all the crystalline starch was described by the XRD crystal-defect fitting.  
221 Then, the difference in the percentage between amorphous starch calculated from XRD

222 and that from  $^{13}\text{C}$  CP/MAS NMR was considered to be due to the mobile amorphous  
223 starch.

224

### 225 2.3.3. *Tensile testing*

226 Tensile tests were performed with an Instron<sup>®</sup> 5543 universal testing machine  
227 (Instron Pty Ltd, Bayswater, Vic., Australia) with a 500 N load cell on dumbbell-shaped  
228 specimens cut from the sheets with a constant deformation rate of 10 mm/min at room  
229 temperature. The specimens corresponded to Type 4 of the Australian Standard AS  
230 1683:11 (ISO 37:1994), and the testing section of each specimen was 12 mm in length  
231 and 2 mm in width. Young's modulus ( $E$ ), tensile strength ( $\sigma_t$ ), and elongation at break  
232 ( $\varepsilon_b$ ) were determined by the Instron<sup>®</sup> computer software, from at least 7 specimens for  
233 each of the plasticised starch samples.

234

### 235 2.3.4. *Dynamic mechanical thermal analysis (DMTA)*

236 Dynamic mechanical thermal analysis (DMTA) was performed on rectangular  
237 sections taken from tensile bars of the plasticised starch samples using a Rheometric  
238 Scientific<sup>™</sup> DMTA IV machine (Rheometric Scientific, Inc., Piscataway, NJ, USA) in  
239 the dual cantilever bending mode from  $-100$  to  $110$  °C, with a heating rate of 3 K/min, a  
240 frequency of 1 Hz, and a strain value of 0.05%. The dynamic storage modulus ( $E'$ ), loss  
241 modulus ( $E''$ ), and loss tangent ( $\tan \delta = E''/E'$ ) were obtained. To prevent water  
242 evaporation during the measurements, the specimens were coated with Vaseline grease.  
243 No swelling of the specimens was observed, suggesting no adverse effect of the Vaseline.

244

245 2.3.5. *Thermogravimetric analysis (TGA)*

246 A Mettler Toledo TGA/DSC1 machine (Mettler-Toledo Ltd., Port Melbourne, Vic.,  
247 Australia) was used with 40  $\mu$ L aluminium crucibles for thermogravimetric analysis  
248 (TGA) under nitrogen. A sample mass of about 5 mg was used for each run. The  
249 samples were heated from 25  $^{\circ}$ C to 550  $^{\circ}$ C at 3 K/min.

250

251 2.3.6. *Electrical conductivity*

252 Volume resistivity measurements were performed on the different starch-based films.  
253 The resistivity of samples (circular with diameter of 60 mm) was measured in triplicate  
254 using a Keithley electrometer (Model 6517A, Keithley Instruments, Inc., Cleveland, OH,  
255 USA) equipped with an 8009 test fixture and employing the Keithley Alt-Polarity method.  
256 The sample of interest was placed between two annular electrodes and the volume  
257 resistivity measured by applying a DC voltage potential across opposite sides of the  
258 sample and measuring the resultant current through the sample. This test conforms to  
259 ASTM D-257. The corresponding electrical conductivity values were obtained as the  
260 inverse of the volume resistivity values.

261

262 **3. Results and Discussion**

263 3.1. *Moisture contents*

264 While different formulations were used for preparing the samples, the water contents  
265 in the final samples could be largely varied by compression moulding and conditioning.  
266 Table 1 shows that the final water content was both affected by the original IL content  
267 and the RH during conditioning, but not the starch type — generally for both starches a

268 higher IL content and/or a higher RH during conditioning could lead to a higher final  
269 water content. It is noteworthy that except G80-27-H and RMS-27-H, the final water  
270 contents were lower than the water contents in original formulations, meaning that water  
271 desorption occurred during conditioning for most of the samples. This could suggest that  
272 there were very strong interactions between the IL and the starch, so both of them had  
273 much smaller chance to interact with water. In this case, the free water could mostly  
274 evaporate to the environment during the long-time conditioning. Unlike previous studies  
275 of solutions of starch, water and [Emim][OAc] (Mateyawa et al., 2013) where  
276 preferential interactions between water and the IL were proposed, the current work  
277 involves formulations containing starch as the main component for melt processing.  
278 Thus, although the water-[Emim][OAc] mixture was initially added into the starch (and  
279 strong interactions between [OAc<sup>-</sup>] anions and water could firstly form (Hall et al.,  
280 2012)), during conditioning the IL might change to preferably interact with the abundant  
281 starch hydroxyls, resulting in its dissociation with water. Previous studies have suggested  
282 that IL anions could act as proton acceptors to form hydrogen bonding with the  
283 biopolymer hydroxyls (Abe, Fukaya, & Ohno, 2012; Fukaya, Sugimoto, & Ohno, 2006;  
284 Remsing, Swatloski, Rogers, & Moyna, 2006; Zhang et al., 2014). Nonetheless, the  
285 mechanism for the change of interactions shown in the current work is worth further  
286 investigation.

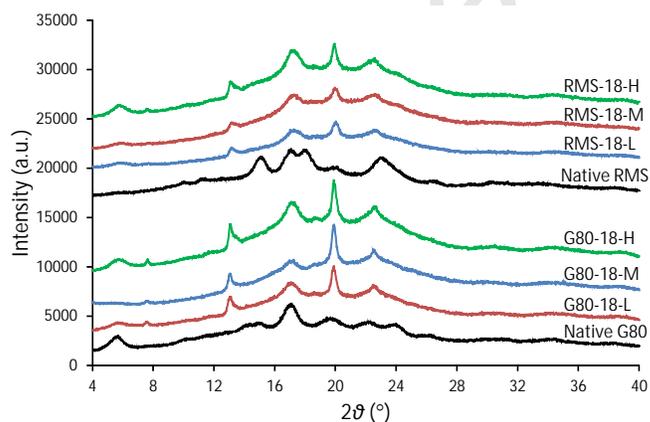
287

### 288 3.2. *Structural characteristics*

289 Figure 1 shows the XRD patterns of the two native starches and their plasticised  
290 samples. Native G80 showed a strong diffraction peak at a  $2\theta$  position of around  $17^\circ$ ,

291 with a few smaller peaks at  $2\theta$  of approximately  $5^\circ$ ,  $10^\circ$ ,  $14^\circ$ ,  $15^\circ$ ,  $19^\circ$ ,  $22^\circ$ ,  $23^\circ$ ,  $26^\circ$ ,  $31^\circ$ ,  
 292 and  $34^\circ$ , indicative of B-type crystalline structure (Cheetham & Tao, 1998; Tan et al.,  
 293 2007). After processing, besides the original B-type characteristic peaks (main peak at  
 294  $2\theta \approx 17^\circ$ ), all the starch samples displayed peaks at  $2\theta$  of around  $7^\circ$ ,  $13^\circ$ ,  $20^\circ$ , and  $22^\circ$ ,  
 295 characteristic of  $V_H$ -type crystalline structure, a single-helical amylose structure (similar  
 296 to that formed by amylose–lipid helical complexes) and is well known for thermally-  
 297 processed (e.g., compression moulding and extrusion) starch-based materials (van Soest  
 298 et al., 1996). That is, the plasticised samples contained crystalline structure not  
 299 destructured by compression moulding (which is normal in starch processing) and some  
 300 newly formed  $V_H$ -type crystalline structure mainly induced by processing (and possibly  
 301 also some newly formed B-type crystalline structure during ageing with moisture) (van  
 302 Soest et al., 1996; van Soest & Borger, 1997).

303



304

305 Figure 1 XRD results of G80 and RMS native starches and the different starch-based  
 306 films. “L”, “M”, and “H” (shown by different colours) correspond to samples  
 307 after conditioning at low (33%), medium (52%) and high (75%) relative  
 308 humidity.

309

310

311 On the other hand, it can be seen from Figure 1 that native RMS showed typical A-  
312 type pattern, with strong reflections at  $2\theta$  of about  $15^\circ$  and  $23^\circ$  and an unresolved doublet  
313 at  $2\theta$  of  $17^\circ$  and  $18^\circ$ , with a few weak peaks at  $2\theta$  of about  $26^\circ$ ,  $30^\circ$ , and  $33^\circ$  (Cheetham  
314 & Tao, 1998; Tan et al., 2007). For the plasticised samples, the doublet at  $2\theta$  of  $17^\circ$  and  
315  $18^\circ$  disappeared, suggesting a complete loss of A-type pattern. Besides, the plasticised  
316 samples displayed strong  $V_H$ -type pattern as shown by sharp peaks at  $2\theta$  of  $7^\circ$ ,  $13^\circ$ ,  $20^\circ$ ,  
317 and  $22^\circ$  (van Soest et al., 1996), and B-type pattern as indicated by strong reflections at  
318  $2\theta$  of  $5^\circ$  and  $17^\circ$  (Cheetham & Tao, 1998; Tan et al., 2007). As for the plasticised G80  
319 samples, the plasticised RMS has both (newly formed)  $V_H$ -type and B-type crystalline  
320 structures.

321 Table 2 shows the contents of double-helices (A- or B-type crystalline structure),  
322 single-helices (V-type crystalline structure), and amorphous parts of the plasticised starch  
323 samples as measured by XRD and NMR. Native G80 has a degree of crystallinity of  
324 32.2%, and this value was greatly reduced in the processed and plasticised samples.  
325 Native RMS has a higher degree of crystallinity, 39.5%, which also decreased  
326 significantly after processing. The plasticised G80 samples overall had a higher degree  
327 of total crystallinity compared with the RMS samples. This could be because of the  
328 higher amount of double-helices remaining (and/or formed during processing), and the  
329 higher content of V-type crystalline structure formed in the plasticised G80 samples.  
330 However, for both starches no apparent difference in total crystallinity could be seen as a  
331 result of the different conditioning RHs, although the diffraction peaks were sharper after

332 higher RH conditioning, showing that crystallites within the sample were either larger or  
333 more perfect. It could be possible that the IL, which was more effective in the interaction  
334 with starch, governed the disruption of original crystalline structure as well as the  
335 formation of new crystalline structure, making the effect of environmental RH, and thus  
336 the sample water content, much less important. Moreover, it can be seen from Table 2  
337 that the G80-based films had a higher mobile amorphous component (%) than that of the  
338 RMS films. As the sample water content was not apparently affected by the starch type,  
339 the differences in mobile amorphous component could be associated with the higher  
340 amylose content in G80. When plasticised by the IL, the linear amylose molecules could  
341 be more mobile than the highly short-branched amylopectin molecules. The more rigid  
342 molecular structure of amylopectin has already been proposed elsewhere (Liu, Halley, &  
343 Gilbert, 2010; Xie et al., 2009).

344

345

346 [Insert Table 2 here]

347

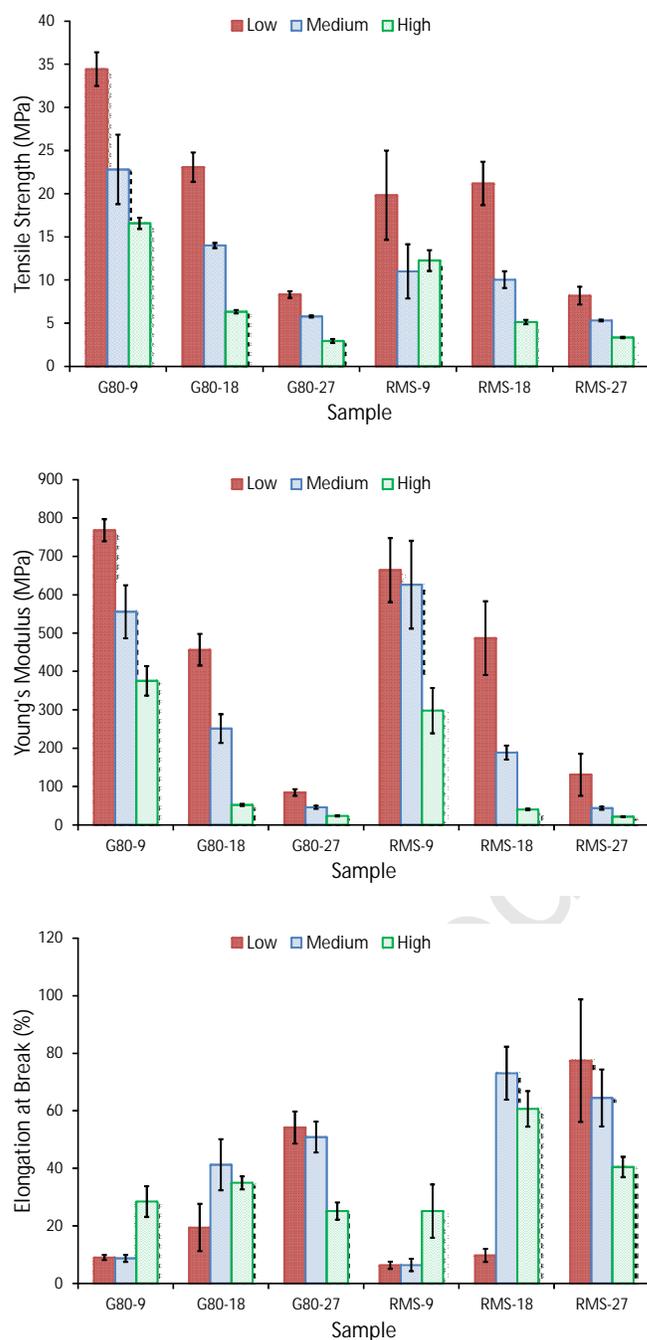
348

### 349 3.3. *Mechanical properties*

350 Figure 2 shows the tensile mechanical properties of the different starch samples. A  
351 higher content of [Emim][OAc] contributed to lower  $\sigma_t$  and  $E$ , as reported previously  
352 (Xie et al., 2014). In addition,  $\sigma_t$  and  $E$  also decreased as the RH (and thus the sample  
353 water content) increased. Since XRD and NMR results have already shown the  
354 insignificance of RH on starch molecular and crystalline orders and that crystallinity was

355 mostly low, the trend observed here is most likely due to the plasticisation effect of  
356 [Emim][OAc] and water (although [Emim][OAc] might be more important based on the  
357 discussion on moisture contents). Both the IL and water could disrupt hydrogen bonding  
358 between starch molecules, and form hydrogen bonding with the –OH sites of starch,  
359 resulting in reduced strength and stiffness. Additionally, there was little apparent effect  
360 of amylose content on  $\sigma_t$  or  $E$  (noting that with certain formulations and conditioning  
361 RHs, the final water contents were quite similar in different amylose-content samples)  
362 except that G80-9 had higher  $\sigma_t$  values than those of RMS-9. It is proposed that when the  
363 material is well plasticised, the macromolecular structure (amylose or amylopectin) plays  
364 a minor role in determining mechanical properties. That is, the entanglement of  
365 macromolecules (mainly amylose) is not a major influence on mechanical properties.

366



367

368 Figure 2 Tensile strength ( $\sigma_t$ ) (upper), Young's modulus ( $E$ ) (middle), and elongation at  
 369 break ( $\epsilon_b$ ) (lower) of the different starch-based films. The error bars represent  
 370 standard deviations. "Low", "Medium", and "High" (shown by different  
 371 colours and patterns) correspond to samples after conditioning at low (33%),  
 372 medium (52%) and high (75%) relative humidity.

373

374

375 The  $\varepsilon_b$  value was also affected by the RH (and thus the sample water content), but in a  
376 more complex way. It was observed from Figure 2 that increase in RH could either  
377 increase or decrease  $\varepsilon_b$ , depending on [Emim][OAc] content. When the [Emim][OAc]  
378 content was 18 wt.%, increase in RH initially increased  $\varepsilon_b$  remarkably and then decreased  
379 this value to some extent. Nevertheless, when the [Emim][OAc] content was 27%,  
380 increase in RH from 33% to 75% decreased  $\varepsilon_b$  progressively. It is proposed that the IL  
381 could disrupt starch H-bonding and prevent macromolecular entanglement, making the  
382 polymer have less “connections” between its chains and become “weaker”. And also  
383 when the material was “softened” too much by plasticisation, there was no work  
384 hardening to stabilise drawing, as indicated by increased  $\varepsilon_b$ . In addition, it can be noticed  
385 that when the material was well plasticised but not “too soft” (the [Emim][OAc] content  
386 18%), RMS could lead to a higher value of  $\varepsilon_b$  than that for G80. This differs from the  
387 results of extruded starch-based films that show higher  $\varepsilon_b$  in starch with a higher amylose  
388 content (Li et al., 2011). Here with, again, much less entanglement of macromolecules  
389 (mainly amylose) due to the plasticisation by [Emim][OAc], the major reason accounting  
390 for the moderately higher  $\varepsilon_b$  for the RMS samples might be the much bigger size of  
391 amylopectin macromolecules which could be stretched more before breaking.

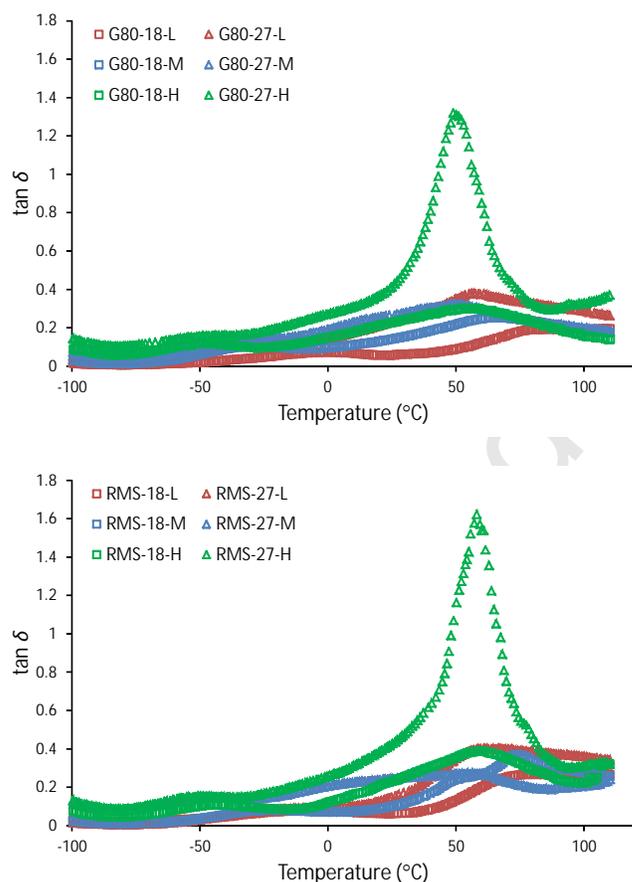
392

### 393 3.4. DMTA analysis

394 Figure 3 shows the DMTA results of the different starch samples. For some of the  
395 samples, a prominent peak was shown between 30 °C and 100 °C. Based on previous

396 studies (Madrigal, Sandoval, & Müller, 2011; Perdomo et al., 2009), this peak can be  
 397 attributed to the glass transition of starch ( $T_g$ ), which will be the main focus of the  
 398 discussion below. Prior to this peak, another moderate peak can be seen at a lower  
 399 temperature (between  $-80$  °C and  $30$  °C depending on sample) which can be ascribed to  
 400 the glass transition of plasticiser-rich domains.

401



402

403 Figure 3  $\tan \delta$  of the different starch-based films (top: G80; bottom: RMS). “L”, “M”,  
 404 and “H” (shown by different colours) correspond to samples after conditioning  
 405 at low (33%), medium (52%) and high (75%) relative humidity.

406

407

408 It can be seen from Figure 3 that, for both G80 and RMS, the samples with 27 wt.%  
409 [Emim][OAc] content normally had lower  $T_g$  than those with 18 wt.% [Emim][OAc], but  
410 a more intense peak height. This could be attributed to the greater plasticisation effect of  
411 [Emim][OAc] relative to that of water (Xie et al., 2014). For the samples conditioned at  
412 low and medium RH, there was a big difference in how the  $T_g$  varied with [Emim][OAc]  
413 content (cf. Table 3). For example, for the plasticised G80 samples conditioned at low  
414 RH,  $T_g$  with 18 wt.% [Emim][OAc] content was 79 °C, which decreased to 57 °C when  
415 the [Emim][OAc] content was increased to 27 wt.%. For the RMS samples conditioned  
416 at low RH,  $T_g$  was 76 °C with 18 wt.% [Emim][OAc] content, while  $T_g$  was 61 °C with  
417 27 wt.% [Emim][OAc] content. For both starch samples conditioned at high RH, when  
418 the [Emim][OAc] content was 18 wt.%, the peak height was still at a level comparable to  
419 those in the cases discussed above; however, when the [Emim][OAc] content was  
420 changed to 27 wt.%, a strong and sharp peak representing the glass transition of starch  
421 was observed. This apparent transition could be associated with the greater mobility  
422 assisted by the highest contents of both [Emim][OAc] and water (resulting from high  
423 RH). Nonetheless, for the samples conditioned at high RH (thus with the highest water  
424 contents), when the [Emim][OAc] content was changed from 18 wt.% to 27 wt.%,  $T_g$  did  
425 not vary much, from 52 °C to 49 °C for G80 and from 59 °C to 58 °C for RMS. It is  
426 proposed that once the starch macromolecules are saturated with plasticisers, further  
427 addition of plasticiser will not change the molecular mobility (reflected by  $T_g$ ) any further.

428

429

430 [Insert Table 3 here]

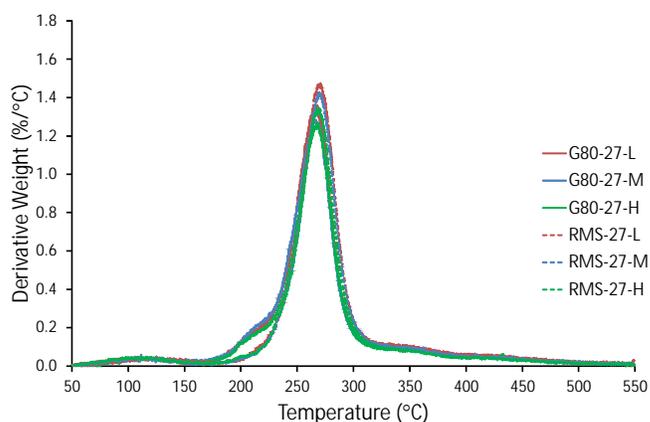
431

432

## 433 3.5. TGA

434 Our previous report has shown that [Emim][OAc] has an obvious effect in reducing  
435 the thermal decomposition temperature of starch-based materials (Xie et al., 2014). The  
436 effects of conditioning RH and amylose content were further investigated here and the  
437 results are shown in Figure 4. It can be seen that all samples had a major derivative  
438 weight percentage peak between 200 °C and 350 °C, after a gentle hump ranging from  
439 50 °C to 170 °C. The large peak can be associated with the breakage of long chains of  
440 starch as well as the destruction (oxidation) of the glucose rings (Liu, Yu, Liu, Chen, &  
441 Li, 2009b), while the smaller hump can be ascribed to moisture loss from the samples.  
442 For the RMS samples, there seemed to be a small shoulder peak between 190 °C and  
443 230 °C, which overlapped with the major peak. This peak can be specifically ascribed to  
444 the breakage of starch long chains (Liu et al., 2009b). With a lower amylose/amylopectin  
445 ratio (increased molecular weight), this peak moves to a higher temperature, thus merging  
446 into the major peak (Liu et al., 2009b). Therefore, for RMS, this small peak could not be  
447 seen. Besides this small peak, the results here show no apparent difference in the thermal  
448 stability between the samples of different amylose contents as well as those with different  
449 water contents (conditioned at different RHs), which is similar to the results for starch  
450 with only water (Liu et al., 2009b).

451



452

453 Figure 4 TGA results of the different starch-based films. “L”, “M”, and “H” (shown by  
 454 different colours) correspond to samples after conditioning at low (33%),  
 455 medium (52%) and high (75%) relative humidity.

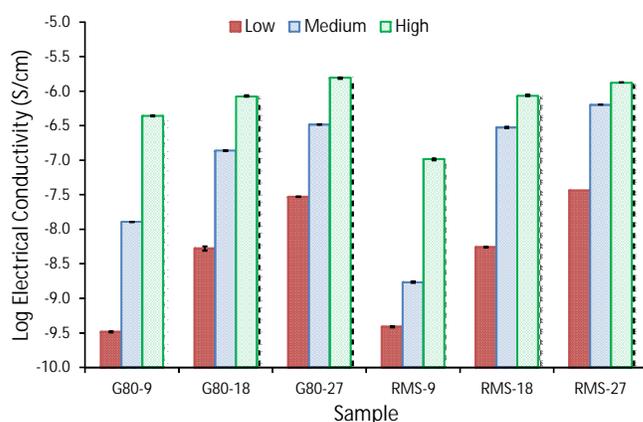
456

457

### 458 3.6. *Electrical conductivity*

459 The electrical conductivity results for the different samples are shown in Figure 5. It  
 460 can be seen that the electrical conductivity ranged between  $10^{-9.5}$  to  $10^{-5.8}$  S/cm for  
 461 different formulations. Wang et al. (2009a) prepared starch-based films plasticised by  
 462 30 wt.% 1-allyl-3-methylimidazolium chloride ([Amim][Cl]), which had electrical  
 463 conductivity as high as  $10^{-1.6}$  S/cm at 14.5 wt.% water content. Sankri et al. (2010)  
 464 showed that starch-based films plasticised by 30 wt.% 1-butyl-3-methylimidazolium  
 465 chloride ([Bmim][Cl]) had electrical conductivity of  $10^{-4.6}$  S/cm at 13 wt.% water content.  
 466 Sankri et al. (2010) further proposed that the high electrical conductivity obtained by  
 467 Wang et al. (2009a) may be explained by increased ion mobility due to the ion pair  
 468 dissociation mechanism described by Zhang et al. (2005), and this ion pair dissociation  
 469 might not be apparent for [Amim][Cl] resulting in more localised ions in the case of

470 [Amim][Cl]-plasticised starch. Also, as the conductivity is mainly controlled by ion  
 471 diffusivity and mobility, the anion should be small, with delocalized charge. For the  
 472 lower electrical conductivity of [Emim][OAc]-plasticised starch in this study as  
 473 compared to those of starch-based materials plasticised by other ILs in the literature, the  
 474 lower extent of ion pair dissociation and the anion size might be a reason, while the  
 475 smaller amount ( $\leq 27\%$ ) of IL in starch should also be considered.  
 476



477

478 Figure 5 Electrical conductivity of the different starch-based films. The error bars  
 479 represent standard deviations. “Low”, “Medium”, and “High” (shown by  
 480 different colours and patterns) correspond to samples after conditioning at low  
 481 (33%), medium (52%) and high (75%) relative humidity.

482

483

484 From Figure 5, a general trend could be identified in that both increase in RH and  
 485 [Emim][OAc] content could increase the electrical conductivity, with the effect of RH  
 486 being more significant. Wang et al. (2009a) have indicated that increasing ion  
 487 concentration by increasing the IL content could improve the conductance of plasticised

488 starch films effectively, and high water content can be advantageous to the transference  
489 of the anions and cations in plasticised starch films. Nevertheless, there was no apparent  
490 trend regarding the influence of amylose content on electrical conductivity. The  
491 plasticised G80 samples with 9% [Emim][OAc] content conditioned at the medium and  
492 high RH seemed to have higher electrical conductivity than the plasticised RMS samples  
493 with the same [Emim][OAc] content conditioned at the same RHs. But this may need  
494 further investigation.

495

#### 496 **4. Conclusion**

497 It is well established in the literature that the amylose content of starch can greatly  
498 influence the structure and properties of starch-based materials. However, this study  
499 showed that the amylose content could only have some degree of influence on the  
500 crystalline structure and the mobility of the amorphous chain segments in [Emim][OAc]-  
501 plasticised starch. Nevertheless, this structural difference was shown to not significantly  
502 impact on mechanical properties, glass transition temperature, thermal stability, nor  
503 electrical conductivity of plasticised starch films. This may be ascribed in part to the  
504 relatively low degree of crystallinity in the starch samples, meaning that the plasticisation  
505 of starch macromolecules by [Emim][OAc] and water could play a major role in  
506 determining material characteristics. Furthermore, the strong plasticisation effect  
507 imparted by [Emim][OAc] compared to other plasticisers could make entanglement of  
508 starch macromolecules (mainly amylose) much less significant. As a result, rather than  
509 the IL content, RH conditioning and thus the sample water content predominantly

510 influenced mechanical properties, glass transition temperature, and electrical  
511 conductivity.

512 Overall, this study suggests that, with the strong plasticisation effect of an IL, the  
513 effect of amylose content on characteristics of starch-based materials could become  
514 unimportant, thus the use of relatively more expensive high-amylose starches can be  
515 unnecessary for the formation of mechanically-useful structures in biomaterials  
516 applications. This study also shows the potential of IL-plasticised starch-based materials  
517 in applications as smart devices where the control of material characteristics by  
518 environmental RH is desirable.

519

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528

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715 **Figure captions**

716 Figure 1 XRD results of G80 and RMS native starches and the different starch-based  
717 films. “L”, “M”, and “H” (shown by different colours) correspond to samples  
718 after conditioning at low (33%), medium (52%) and high (75%) relative  
719 humidity.

720 Figure 2 Tensile strength ( $\sigma$ ) (upper), Young’s modulus (E) (middle), and elongation at  
721 break ( $\epsilon_b$ ) (lower) of the different starch-based films. The error bars represent  
722 standard deviations. “Low”, “Medium”, and “High” (shown by different  
723 colours and patterns) correspond to samples after conditioning at low (33%),  
724 medium (52%) and high (75%) relative humidity.

725 Figure 3  $\tan \delta$  of the different starch-based films (top: G80; bottom: RMS). “L”, “M”,  
726 and “H” (shown by different colours) correspond to samples after conditioning  
727 at low (33%), medium (52%) and high (75%) relative humidity.

728 Figure 4 TGA results of the different starch-based films. “L”, “M”, and “H” (shown by  
729 different colours) correspond to samples after conditioning at low (33%),  
730 medium (52%) and high (75%) relative humidity.

731 Figure 5 Electrical conductivity of the different starch-based films. The error bars  
732 represent standard deviations. “Low”, “Medium”, and “High” (shown by  
733 different colours and patterns) correspond to samples after conditioning at low  
734 (33%), medium (52%) and high (75%) relative humidity.

735

736 **Tables**

737 Table 1 Samples codes, formulations, and relative humidity during conditioning, of the starch-based films.

Code	Formulation <sup>a</sup>					Conditioning
	Starch type	Starch content <sup>b</sup>	[Emim][OAc] content	Water content (original) <sup>c</sup>	Water content (post-conditioning)	Relative humidity (%)
G80-9-L	Gelose 80	85.9	9	35.1	7.60±0.29 <sup>d</sup>	33
G80-9-M		85.9	9	35.1	11.35±0.18	52
G80-9-H		85.9	9	35.1	14.22±0.20	75
G80-18-L		85.9	18	26.1	7.36±0.18	33
G80-18-M		85.9	18	26.1	12.88±0.12	52
G80-18-H		85.9	18	26.1	20.12±0.16	75
G80-27-L		85.9	27	17.1	8.94±0.08	33
G80-27-M		85.9	27	17.1	17.16±0.14	52
G80-27-H		85.9	27	17.1	27.94±0.24	75
RMS-9-L	Regular maize starch	85.6	9	35.4	8.34±0.05	33
RMS-9-M		85.6	9	35.4	11.78±0.27	52

RMS-9-H	85.6	9	35.4	14.87±0.25	75
RMS-18-L	85.6	18	26.4	8.00±0.11	33
RMS-18-M	85.6	18	26.4	12.35±0.11	52
RMS-18-H	85.6	18	26.4	20.69±0.08	75
RMS-27-L	85.6	27	17.4	9.04±0.08	33
RMS-27-M	85.6	27	17.4	15.96±0.22	52
RMS-27-H	85.6	27	17.4	27.84±0.06	75

738 <sup>a</sup> Portions in weight; <sup>b</sup> Dry weight; <sup>c</sup> Combination of added water and original moisture content in starch; <sup>d</sup> Standard deviation

739

740 Table 2 XRD and  $^{13}\text{C}$  CP/MAS NMR results of the starch-based films

Sample	XRD Results			$^{13}\text{C}$ CP/MAS NMR Results			
	Double helix	V-type	Amorphous	Double helix	V-type	Rigid amorphous	Mobile amorphous
Native G80	32.2	ND <sup>a</sup>	–	–	–	–	–
G80-18-L	22.4	8.4	69.2	20.0	10.8	41.6	27.6
G80-18-M	18.4	9.4	72.2	17.5	10.3	46.3	25.9
G80-18-H	21.2	8.2	70.5	20.4	9.1	48.6	21.9
Native RMS	39.5	ND <sup>a</sup>	–	–	–	–	–
RMS-18-L	19.7	4.8	75.5	17.7	6.8	60	15.5
RMS-18-M	18	4.8	77.2	15.9	6.9	57.1	20.1
RMS-18-H	18.4	5.1	76.5	17.5	6.0	57.9	18.6

741 <sup>a</sup> Unable to be determined as the V-type crystallinity pattern was difficult to be differentiated from the A or B-type crystallinity pattern

742

743 Table 3 Glass transition temperatures ( $T_g$ ) of the starch-based films

Sample	$T_g$ (°C)
G80-18-L	79
G80-18-M	63
G80-18-H	52
G80-27-L	57
G80-27-M	52
G80-27-H	49
RMS-18-L	76
RMS-18-M	73
RMS-18-H	59
RMS-27-L	61
RMS-27-M	56
RMS-27-H	58

744

745

745 **Highlights:**

- 746 ✓ An ionic liquid, [Emim][OAc], was used to make plasticised starch-based materials
- 747 ✓ [Emim][OAc] made the starch structural effect (amylose/amylopectin) insignificant
- 748 ✓ [Emim][OAc] had a strong plasticization effect on regular and high-amylose starches
- 749 ✓ The material characteristics were mainly affected by its moisture content
- 750 ✓ The moisture content had a great impact on the mechanical properties and electro-
- 751 conductivity

752

753